

TECHNOLOGY UTILIZATION REPORT

Technology Utilization Division

SOME NEW METAL AND METAL-CERAMIC COMPOSITES

GPO PRICE \$.25

CFSTI PRICE(S) \$ _____

Hard copy (HC) _____

Microfiche (MF) 150

ff 653 July 85



FACILITY FORM 602

N67 13531
(ACCESSION NUMBER)31
(PAGES)

(NASA CR OR TMX OR AD NUMBER)

(THRU)

1
(CODE)15
(CATEGORY)

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

TECHNOLOGY
UTILIZATION REPORT

Technology
Utilization
Division

SOME NEW METAL AND
METAL-CERAMIC COMPOSITES

Prepared under contract for NASA by
SAMUEL KORMAN
RAI Research Corp., Long Island City, N.Y.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

WASHINGTON, D.C.

1966

NOTICE • This document was prepared under the sponsorship of the National Aeronautics and Space Administration. Neither the United States Government nor any person acting on behalf of the United States Government assumes any liability resulting from the use of the information contained in this document, or warrants that such use will be free from privately owned rights.

For Sale by the Superintendent of Documents,
U.S. Government Printing Office, Washington, D. C. 20402
Price: 25 cents
Library of Congress Catalog Card Number 66-61783

Foreword

The Administrator of the National Aeronautics and Space Administration has established a Technology Utilization Program for "the rapid dissemination of information . . . on technological developments . . . which appear to be useful for general industrial application." From a variety of sources, such as NASA research centers and NASA contractors, space-related technology is screened, and that which has potential industrial use is made generally available.

This publication is one of a series issued to provide such technological information. It was designed to show industrial management the current state of development of some kinds of composites consisting of metal components and metal-ceramic components. The text presents only limited information because the main purpose is to disclose basic concepts, objectives, and avenues of availability which characterize these composite materials as emergent engineering materials of broad potential applicability. Clarification of these aspects for the educated layman

confronted with nonspace technical objectives may encourage further development and use of new composites in the national industrial complex.

Significant NASA contributions to the exploitation of metal and metal-ceramic composite materials have included (1) development of production technology, (2) study of the properties and service behavior of composites, and (3) advancement of the theory and design considerations of composites as engineering materials.

By its pioneering investigations into dispersion-strengthening and fiber-matrix relationships, NASA has promoted the rational design of composites for structural application. The opening chapter describes the need for such work as part of the space effort. Subsequent chapters give some information on dispersion-strengthened, fiber-matrix, and reinforced ceramic systems. Some representative applications for composites and various constituents are also briefly discussed.

GEORGE J. HOWICK, *Director
Technology Utilization Division,
National Aeronautics and
Space Administration*

Contents

	Page
Chapter 1. Classification and Definition of Composites	1
2. Dispersion-Strengthened Composites	6
3. Fiber Composites	13
4. Reinforced Ceramics	22

Bibliography

Sources of Fundamental Discussions	24
Publications Citing NASA-Sponsored Work	24
Commercial Sources of Composites and Composite Materials	25

Classification and Definition of Composites

This report was written to define a portion of the emergent composites field in which space programs have the Nation's technological and scientific capability; to describe the contribution thus made to a closer and more general understanding of the underlying basis for interest in composites; and to suggest the benefits which can accrue to the national economy from this technical work sponsored by the National Aeronautics and Space Administration.

Growth of knowledge in the aerospace field is so rapid and diversified that a systematic exposition of the details can become obsolete and incomplete while being compiled. Interest in composites has spread rapidly. It is difficult even now to define composites in a manner not so general as to lack usefulness and yet sufficiently inclusive to expedite use of advances in space technology in other fields. We have, for example, been told:

1. Composites are artificial (manmade) materials produced by joining two or more materials to derive advantages from certain properties of each and to overcome disadvantages arising from deficiencies of each when used separately.

2. Composites are divisible into matrix systems, laminates, and sandwich structures; matrix systems contain a particulate, flake, fiber, whisker, or combination of such discrete phases embedded in a continuous phase, while laminates are bonded layers of different materials, and sandwich structures have a low-density core such as a honeycomb or foam, usually between two higher density sides.

3. Composites are nothing new, they are found in nature, they can be structures as well as materials.

4. A composite material is a materials system composed of a mixture or combination of two or more macroconstituents that differ in form and/or material composition and that are essentially insoluble in one another.

5. A composite is something that comes apart at the interfaces.

6. A composite is a mixture of two or more materials that has to be produced in a certain way.

Each definition is technically or qualitatively inadequate in some respect. All of these definitions point in a certain direction which is worth emphasizing: more than one kind of substance is involved. Hence we are required to consider more than one set of property values. To whatever extent two or more materials are present in the system, the net effect of their individual collateral properties and the effect of interaction between them will comprise the properties of the system as a whole. Since we are not concerned with aesthetic aspects, the kind of definition which would make sense for us would be based upon the properties of the system as a whole—in short, a functional definition.

CLASSIFICATION OF COMPOSITES

For whatever purposes a composite system of materials is assembled, each component is usually detectable as a discrete phase at some level. In certain cases a microscope is needed; in others the difference in phases is apparent to the eye. The mode of observation is secondary to the achievement of some enhancement of properties as a result of the combination. Sometimes there are limitations on the availability of components in

regard to physical characteristics such as size and shape, which impede the attainment of theoretically conceivable design criteria and properties. This is often the result of inadequate production technology, processing considerations in the compositing steps, and sometimes undesirable interactions between the components at the interface during service.

Workers in the composites field accept the challenge because of the potential results. The hope is that superior serviceable results can be obtained by deliberate design based on understanding of the phenomena noted when materials are combined. Many men believe that composites contain the answer to the dream of materials with tailor-made properties. For many purposes, such as high-performance aerospace vehicles, this objective is becoming virtually inescapable. The materials bottleneck appeared very early in the development of aircraft, space vehicles, and missile technology, and has highly respected analogs in industry.

In general, the components of a composite are present in unequal quantities. When we ignore the functional aspects, the relationship of constituents is physical—or, exactly, structural—and five classes of composites are readily identifiable.

1. Fiber composites, in which at least one constituent has a high ratio of length to diameter, as in a continuous or chopped filament, or a whisker. (The term is derived from a production method in which the fibers appear like whiskers covering a surface.) Another constituent may be shapeless and may form a continuous matrix in which the first one is embedded.

2. Particulate composites, in which one constituent is in the form of very small relatively uniformly shaped particles, usually on the order of microscopic dimension embedded in a continuous matrix.

3. Flake composites, in which one constituent has the physical shape of a flat particle (i.e., relatively isotropic in two of three dimensions) embedded in a matrix of the other constituent.

4. Filled composites, in which one constituent forms a matrix which has a proliferation of channels, cells, or compartments that are filled with another constituent.

5. Laminar composites, consisting of layers of single constituents bonded together along two-dimensional areas of contact.

From this structural grouping, a fact of profound significance emerges: the heterogeneous nature of the composite, with discrete constituent phases, necessitates consideration of a surface of contact or interface. The interface is the site of interaction between the two constituents, the place where the properties of one merge, interact, or transfer into the properties of the other. In serving this function, the interface sometimes contains a third constituent which acts as a bonding agent between the other two. The primary general consideration in approaching the functionality of a composite is the insurance of continuity of maximum interface area, so that the superior properties of one or the other constituent may be brought into play most effectively.

BASIS FOR SPECIFIC FUNCTIONAL DEFINITION

Early in the development of high-speed aircraft, aerospace vehicles, and missiles, design engineers were forced to consider heat transfer between some portion of the surface of the flying object and a very much hotter or heat producing fluid. This problem is encountered in the nozzle of the rocket motor and at the surface of a vehicle moving into, or through, the Earth's atmosphere at high velocities. The latter is the classical problem of aerodynamic heating, which may be analyzed briefly in the following way.

Calculation of heat transfer, according to the Reynolds analogy, compares the friction between the solid surface and the moving gas, considered as a transfer of momentum effect, with energy transfer. This occurs between the gas at some given distance outward from the surface and a layer of gas immediately adjacent to the solid surface, the boundary layer. Flow may be laminar

or turbulent. In the former case, energy is transferred by collision processes between molecules, while in the latter the transfer is by eddy diffusivity.

For supersonic velocity at moderate Mach number where the surface is insulated so that no heat transfer occurs, the boundary layer temperature is raised to a peak value, known as the adiabatic stagnation temperature. The analogy being exact for compressible fluids with a Prandtl number of unity, and corresponding to a reduction in the relative gas velocity as the boundary layer is approached, in a manner corresponding to adiabatic compression. Where the Prandtl number is different from unity, the so-called recovery temperature is slightly less.

In a case where the surface is not insulated and heat transfer can occur from the gas to the solid wall, that transfer is proportional to the temperature difference between the recovery temperature and the wall temperature. The significance is that as the Mach number increases, the ratio of the stagnation temperature and the ambient temperature is $1 + M^2/5$, where M = the Mach number. Table 1 indicates some values for this relationship.

TABLE 1.—Stagnation temperature vs. Mach number

Ambient temperature, °K	Mach Number	Stagnation temperature, °K
300	0.7	330
300	1.0	360
300	2.0	540
300	4.0	1 260
300	8.0	4 140
300	16.0	15 700
300	25.0	37 800

This situation becomes even more aggravated in the case of turbulent flow, where the heat-transfer coefficient is larger. At the relatively low Mach number 2.0, the stagnation temperature is beyond the physical endurance of personnel and equipment of classical design. At higher velocities the stagnation temperature rises rapidly to values at which molecular instability sets in

and the surrounding gases become dissociated and ionized; a plasma sheath is then said to have been formed around the body.

A condition of sustained flight—which could be as short as a matter of minutes in sufficiently dense air, as, for example in a gliding reentry of a space vehicle approaching the Earth's surface—often must be reckoned with. In such instances, steady-state radiation temperatures in the thousands of degrees Fahrenheit are attained. Figure 1 illustrates this diagrammatically.

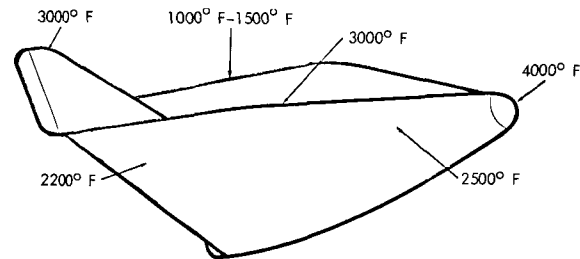


FIGURE 1.—Surface radiation equilibrium temperatures (as given for a reentry glider by E. E. Mathuser, of NASA) are typical of the long-term high-temperature conditions becoming increasingly important in aerospace materials development.

The mission profile of a space vehicle is likely to include a sustained exposure to aerodynamic heating, and one must consider the effects upon the properties of the materials used in constructing and operating the vehicle. Heat effects accompanying the high-speed flow of fluids past solid surfaces must also be considered in many other applications of materials.

THERMAL EFFECTS UPON STRUCTURAL PROPERTIES

To utilize composites of metals, alloys, and ceramics and to extend the useful service regime to higher temperatures and thermal exposure times, it is necessary to review the effects in some detail upon simple metallic structure in respect to individual properties.

To make this perfectly clear, a statement of basic definitions of structural properties is warranted.

When a bar of metal is exposed to loading, it is said to be under stress. The consequent deformation, such as bending or stretching, is termed the "strain," which may be either

permanent or temporary. If they are proportionate, following Hooke's law, the behavior of the metal is said to be in its elastic range. The ratio of stress to strain, or the slope of the curve expressing the relationship, is termed the "modulus of elasticity." There are two kinds of moduli. When the deformation is tensile or compressive, the elastic modulus is called Young's modulus. When the deformation is caused by twisting action, the elastic modulus is known as the shear modulus or modulus of rigidity. As the temperature of the metal bar is raised, the modulus of elasticity is reduced.

When the stress imposed upon the bar of metal reaches a value at which a marked increase in deformation occurs without increase in load, that value is known as the yield point. The maximum load which the bar can withstand prior to fracture represents the ultimate stress, while the fatigue limit or endurance limit is the maximum stress which the bar will stand without fracture where the stress is imposed cyclically. These properties may also be reduced by increased temperature.

When the stress is lower than that corresponding to the normal yield strength, but is maintained for long periods of time, the bar of metal may undergo plastic deformation, known as creep. The rate at which this occurs increases with temperature.

Among the effects of aerodynamic heating upon the materials of construction and equipment of aerospace vehicles (and of human astronauts indirectly) one must consider:

1. Reduction of the modulus of elasticity with increase in temperature. This affects the resistance of structures to buckling and other structural instabilities.

2. Reduction of the yield point, ultimate stress, and fatigue stress with increase in temperature, leading to structural failure.

3. Increase in creep rate with temperature, tending toward buckling and excessive load concentration.

4. Excessive induced thermal stresses caused by uneven thermal expansion of structural components.

5. Loss of stiffness, especially torsional stiffness of wings because of uneven temperature distribution.

6. Catastrophic failure as a result of melting and chemical effects caused by oxidation and high temperature corrosion.

Consideration of these phenomena brings one to the conclusion that a functional definition of composites which could motivate technological advancement, and also lead to more useful understanding of the underlying principles, would stress the uses of composites capable of inhibiting these undesirable effects in space vehicles and elsewhere. By means of the joint properties of at least two different species of materials, we would hope to derive enhancement against two classes of structural performance failure, physical and chemical. Physical failure may result from the first five aerodynamic heating effects listed above, while the chemical type is covered in the sixth category.

Quite obviously, for the thermal-temporal regimes encountered in hypersonic aerospace applications of materials, the structural components must remain solid. Therefore, the structural ingredients referred to are metals and inorganic materials, such as ceramics, since polymer and organic materials exposed to high temperatures generally undergo thermal decomposition or melt at relatively low temperatures.

The other major aspects of functional consideration of composites relate to the potential change of state and chemical effects referred to above. As indicated, the interaction of the vehicle with the environment at high velocities produces heat transfer with stagnation temperatures far in excess of the melting points of known structural materials candidates. It also produces lower temperatures capable of causing equipment failure through destruction of organic compounds such as plastics and electronic wire insulation materials, the melting of solder connections, and the malfunction of equipment inside the vehicle (including the human astronaut) because of a high-temperature coefficient. The general consideration which

covers these contingencies is the removal of transferred heat energy as well as the effective use of heat-insulating materials between the interior compartments of the vehicle and the external surfaces.

Furthermore, it is necessary to appreciate that the heat-transfer source is something much more than an inert fluid at high temperature. As mentioned above, superheated air is involved, and at the temperatures encountered air is an extremely reactive chemical complex. The temperature coefficients of chemical reactions which may occur at the surface of the vehicle are very large. The brilliance of high-speed objects such as meteorites, entering the Earth's atmosphere, and NASA missions have made the man-in-the-street aware of the reentry phenomenon. Here again we are confronted with the question of controlling the heat transfer in a manner which will avoid high-temperature chemical reactions, such as oxidation of the heated surfaces of the vehicle. Thermal protection systems are needed. However, these are considered a separate category of the concept of composites, distinguished from the structural function taken up in this review, because different properties and performance features are involved.

Thus, we arrive at two specific functional definitions of composites. The first definition declares that a composite consists of not less than two constituents of a system of materials drawn from the class of metals, alloys, and inorganic compounds, such as ceramics, which system has as its purpose the employment of selected constituents which, taken together, result in a set of physical properties capable of extending the useful region of temperature and thermal energy transfer beyond that of either constituent alone, when used as a structural component.

The second definition asserts that a composite material comprises not less than two constituents drawn without restriction from the standpoint of composition, but which function to limit the transfer of thermal energy into a structure so that its tempera-

ture below the external surface is within some specified limit, and also may function otherwise to inhibit or significantly reduce the rates of chemical reactions which may occur.

The use of two materials of different form and properties to produce a combined action or function may result in a number of modes of combination of properties:

1. Direct summation of the contribution of each constituent is possible. For example, a colligative property, such as density or volume, would consist of the volume fraction of each constituent multiplied by its density in the pure state.

2. A synergistic interaction of properties may result, wherein the resultant composite material property is not merely a summation, but one in which the presence of each material benefits from that of the other material. For example, the combined properties of a composite can be greater than that of either constituent, as in the case of a wood flour-resin composite or fiber-glass-resin. In particular, we are interested in combining strength in one constituent with toughness in the other.

3. The function performed may be a complex combination of simpler separable functions performed simultaneously, but separately, by each constituent, which is specifically selected for the individual function involved. Frequently, this is achieved by the laminar type of composite, as, for example, the utilization of a refractory metal structural substrate over which an oxidation-resistant ceramic coating has been placed.

To meet space objectives, the properties of materials have been taxed to, and beyond, their practical limit. Weight, strength, and physical property considerations at temperatures not normally encountered have led to the support of research and engineering efforts to evoke ingenious solutions to exceedingly rigorous structural vehicular requirements. This report is mainly concerned with the enhancement of structural performance at high thermal loadings and environments.

Dispersion-Strengthened Composites

In 1950, investigators of the Swiss Aluminum Corp. discovered that when fine-sized, partly oxidized aluminum powder was compacted, sintered, and hot worked (e.g., molded and extruded to narrower diameter), a material was produced having strength properties, at elevated temperatures, far in excess of the best heat-resistant aluminum alloys. This material was named S.A.P. Although it was not the very first dispersion-strengthened composite, it does, perhaps, represent the first composite of the dispersion type and is a prototype. From it a whole generation of specifically designed composites of other metals has been developed, and principles concerning the function and characteristics of each phase or component have been explicitly considered.

In S.A.P., the dispersed phase is a ceramic material, aluminum oxide. The powder is, in accordance with our functional definition, a discrete and significant member of the materials system. The oxide phase exists as a thin film covering every metal particle, and has a thickness of approximately 0.1 micron (0.00004 inch). This film can be produced by grinding the metal powder in an oxygen-containing atmosphere. In general, the metal-powder particles are 70 to 140 microns in diameter, with a bulk weight of 1 gm/cc or more. The oxide content ranges from 6 to 15 percent, as against 1 percent in atomized metal powder of comparable particle size. The particles also have a certain amount of internally contained oxide.

The outstanding properties of S.A.P., for purposes of this discussion, are its mechanical properties at elevated temperatures and its great stability against prolonged heating at temperatures up to 600° C. These prop-

erties are reflected in figure 2. From investigations of these alloys, it has been concluded that the mechanical properties depend not only upon the volume percentage of oxide but also on the fineness of distribution.

One phenomenon which greatly affects the properties of a metallic alloy is recrystallization. The original crystallites of metal which are produced by solidification of the molten charge may be distorted and strained during fabrication of the specimen. When heated, the original crystallites will, at some characteristic temperature, dispel the distortion and dissipate the stored energy representing the cold working of fabrication, by transforming into a new strain-free grain structure.

Recrystallization has not been found in S.A.P. which has more than 7 percent oxide, although it has been observed in alloys containing 1 percent to 3 percent oxide. This means that, in the higher oxide compositions, the recrystallization phenomenon

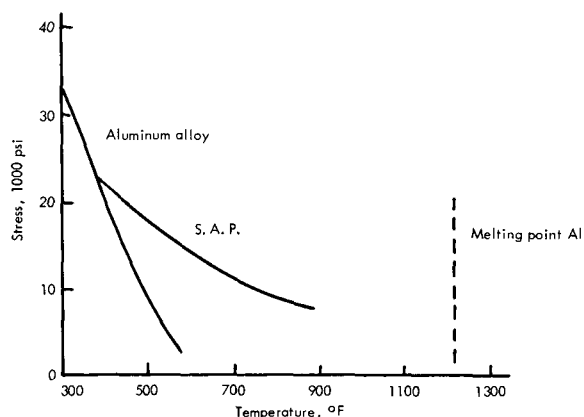


FIGURE 2.—Stress temperature curves for rupture in 1000 hours (after H. C. Cross).

shifts to higher temperatures and the original structure, somehow, is retained after cold working.

These facts about S.A.P. have stimulated many studies of other systems of composites of the dispersion type, with consequent theoretical and technical problems. The successes attendant upon the effort to generalize these results have led to acceptance of a basic principle: such alloys retain their strength at elevated temperatures longer and remain much closer to the melting point than do other types. We will now examine the reasons for this, and discuss the consequences for problems which have arisen in efforts to extend the principle into higher thermal regimes, such as might be useful in aerospace and sophisticated industrial applications.

ANALYSIS OF DISPERSION-STRENGTHENED ALLOY CONCEPT

Earlier in this report we developed a general definition of composites along functional lines. The following discussion in no way detracts from the usefulness of that approach; in fact, it represents a corollary subordinate which will amplify and render its meaning more specific. A dispersion-strengthened alloy is one whose structure consists of a very finely divided dispersed phase, distributed uniformly and randomly within a matrix of a metal (or solid solution alloy), as a result of which, there is a significant augmentation of strength properties of the matrix metal dispersoid combination over that of the matrix alone.

Factors which affect the stability and properties of the alloy include:

- *Solubility of the dispersed phase in the matrix at elevated temperature.*—When the dispersed phase is insoluble, the resultant alloy tends to be stable, as distinguished from alloys which tend to go into solution at elevated temperature and precipitate out on cooling. This action tends to affect the interaction occurring at the interface which is believed to be responsible for the strengthening mechanism.

- *Geometric considerations.*—These include especially the dispersed-phase particle size, the interparticle spacing, and the volume percent of dispersed material. A basic relation involving these parameters has been developed by W. S. Cremens at NASA Lewis Research Center.

$$\text{I.P.} = 4(V/S)^{0.5}(1/f_s - 1)$$

where

I.P. = interparticle spacing
 $(V/S)^{0.5}$ = volume fraction of dispersoid phase in composite alloy
 f_s = ratio of volume to surface area for the dispersed phase in the finished composite alloy

- *Particle shape and distribution, and changes which may occur in either.*

- *Hardness and strength of the dispersed phase.*

- *Structural continuity.*—When based upon resemblance of crystalline character of the two components at the interface brought about by precipitation of the dispersoid, it had a significant bearing upon the properties of the alloy. Similarity of crystal structure between materials on both sides of an interface which permits atomic bonding usually exists in the earliest stages of the formation of a precipitate; local deviation therefrom is referred to as coherency strain. This is difficult to evaluate quantitatively, and is affected by temperature. It is judged indirectly by studying strength properties, such as yield strength and creep. However, many alloys exhibit the strengthening effect when coherency strain has been removed.

- *Interfacial energy.*—This is energy situated at the particle boundary and affecting changes in the dispersion.

- *Stored energy.*—This is energy contained within the body of the alloy as a result of deformation and fabrication. As has been indicated above, dispersed alloys tend to resist the release of such stored energy by the process of recrystallization; this is manifested by a significant rise in the temperature of recrystallization.

● *Fracture strength.*—This is a factor relatively independent of the presence of the dispersed phase, unless the dispersion is capable of inhibiting crack formation by preventing the concentration of forces internally which can lead to cracking.

● *Chemical interactions between the two phases, especially those which can be accelerated by increasing temperature.*—These reactions occur at the interface and can lead to the formation of compounds which can be either beneficial or adverse. Compounds can be produced which have lower melting points than either original phase.

● *Purity of the components.*—This may strongly affect the stability of the composite; the presence of minor alloying agents can adversely affect the stability of the interface,

accelerate diffusion across it, or improve the interfacial bond.

● *Presence of surface films on the particles due to the adsorption of gases and moisture during formation of the composite.*—These can have a profound effect upon the bonding of particles to matrix.

● *Chemical compatibility of the components of the alloy.*—Consideration must be given to corrosion and reaction processes which are favored by the introduction of internal stresses during formation and fabrication of the alloy, and which may become serious at elevated temperature.

In summary, certain generalizations can be emphasized for practical guidance in understanding requirements for successful production of dispersion-strengthened alloys:



FIGURE 3.—Electron micrograph of TD nickel reveals uniform, fine dispersion. This photograph is of a carbon extraction replica taken from an electrolytically etched sample. 6000 \times . (From *Metal Progress*, Dec. 1962, p. 89.)

*1. For significant strength improvement the interparticle spacing should be 1 micron or less, with 0.01 to 0.1 micron considered optimum for a balance of strength, ductility, and resistance to fracture.

2. Particle shape is not clearly understood, but the evidence favors rounded shapes.

3. Greater hardness in the dispersed phase favors greater strength in the alloy.

4. Low interfacial energy favors retention of properties and integrity of the alloy.

5. Factors tending to minimize agglomeration of the dispersed phase are desirable for retention of stability. These include high chemical stability of the dispersed phase, large particle radius, high density and low molecular weight of the dispersed phase—although larger particles tend to reduce mechanical strength by increasing the interparticle spacing, volume fraction, and inhomogeneity of particle distribution.

6. Factors tending to reduce stability include ease of diffusion between phases, high solubility of phases, high interfacial energy, and simplicity of composition of the dispersoid.

7. Purity of materials is essential to avoid nullifying side effects during fabrication. This factor is not always appreciated.

An interesting example of the microscopic appearance of a dispersion-strengthened alloy is shown in figure 3.

THEORETICAL EXPLANATION OF DISPERSION STRENGTHENING

Several attempts have been made to construct a theory which will account quantitatively for the effect of a dispersed phase upon the strength of a metal matrix. These efforts involve modern solid state theory. A report of NASA-sponsored investigations, representing typical and fairly far-reaching applications of the subject, points out that no single approach seems capable of describing the effect upon all the mechanical properties. Hence, the authors undertake to treat selected important properties separately. In particular, emphasis is placed upon the use of solid-state concepts to explain the effect

upon yield strength and upon steady-state constant temperature creep.

Use is made of the behavior of dislocations.¹ Since the yield strength represents a point at which plastic deformation of the solid occurs, this is related to the motion of dislocations. It is postulated that in dispersion-strengthened alloys, the stress required to produce such deformation depends on the force required to move dislocations freely through the matrix. The interaction with dispersed particles is analyzed in a manner which describes with reasonable quantitative results the limitations imposed upon dislocation movement by the size, multiplicity, and spacing of the dispersed particles.

The qualitative picture of the particle-dislocation interaction related to estimation of the yield strength of the alloy suggests that dislocation loops pile up about each dispersoid particle, and that yielding represents the application of forces to this configuration in a manner which results in fracture or plastic deformation of the particle. Quantitatively, the yield strength of the dispersion-strengthened alloy is found to be proportional to the reciprocal square root of the dispersed particle spacing and the square roots of the shear modulus of the dispersed phase and of the matrix metal. Adequate agreement has been found between experimental data relating the yield strength of several types of dispersion-strengthened alloys as a function of dispersion spacing, temperature, and shear modulus of the dispersed phase, as compared with the theoretical model.

The other strength index treated theoretically describes the steady-state creep behavior of dispersion-strengthened alloys. Two models have been analyzed: one for

¹ A dislocation is a vacant atom site or fault in the matrix metal crystal. These sites are capable of motion under the action of applied forces or stresses generated either mechanically or through the influence of thermal diffusion or concentration gradients. A large literature has been developed concerning the dynamics of such motion, as well as the interaction of dislocations with one another and with atoms and agglomerates.

coarse-grained alloys produced by cold-working and subsequent recrystallization, the other for fine grained. Further analysis divides creep behavior into that observable under high and low stresses. The rate-controlling processes involve either so-called dislocation climb or the movement of dislocations around barriers (particles), or the appearance and movement of dislocations at grain boundaries within the metal. Augmented properties such as ductility, fracture, stress to rupture, and work hardening remain unexplained.

PRODUCTION PROCESSES

In principle, dispersion-strengthened alloys may be produced in several ways. It is difficult to find a single process which has universal applicability to all systems with no drawbacks either in the production technology or in the properties of the alloys. Various approaches have been examined in efforts to achieve the strength enhancement obtained with S.A.P. using other metals and dispersoids, particularly those with higher melting points and more refractory properties, as well as maximum stability close to the melting point. These approaches to the production of dispersions within dense metal matrices have been classified as follows.

1. Solid-state transformations, such as precipitation from a supersaturated solid solution and eutectic² decomposition of a solid solution.

2. Gas-liquid reactions, in which oxygen in the ambient atmosphere diffuses rapidly in the liquid state of a binary alloy, which is selectively oxidized internally.

3. Reaction of two liquids to form a new phase in the subsequently solidified metal matrix. An example of this is the mixing of copper-thorium and copper-boron alloys as liquids, in amounts consistent with the formation of a dispersion of thorium boride in

² Eutectic reaction is the reversible reaction of a liquid which forms at constant temperature, two different solid phases during cooling.

copper. This may be followed by casting or by atomizing and consolidation by powder metallurgical methods (compacting, sintering, extrusion), the latter being used to control the size of the dispersions. Another example is the atomization of iron-aluminum alloy to form dispersions of iron-aluminide compound, FeAl_3 , in aluminum. The dispersed phases are not necessarily oxides, but may include hard alloys such as carbides, aluminides, borides, and potentially many other refractory compounds.

4. Liquid-solid reactions, including coprecipitation of mixtures from aqueous solutions. This technique can produce very intimate mixtures and complex salts, which are then dried and selectively reduced, leaving one component in the dispersed oxidized state.

5. Gas-solid reactions, such as reduction of mixed oxides, oxidation and reduction, surface oxidation, and internal oxidation of a dilute alloy. In the case of internal oxidation, one metallic component is selectively oxidized *in situ* by diffusion of oxygen into the alloy at elevated temperature. Examples of this include S.A.P., copper-silicon, copper-aluminum, and nickel-thorium. (It is preferable to carry the oxidation out in the powdered form for effectiveness and uniformity of result.)

6. Mechanical mixing of component powders. This has been used in NASA programs to produce samples for elucidation of subsequent strength factors. It is wholly a powder metallurgical operation, and includes such steps as mixing and blending in ball mills, colloid mills, and blenders, followed by conventional and controlled steps such as compaction, sintering, or hot pressing, and consolidation by metal working such as swaging, hot rolling, and extrusion. All of these steps are straightforward, and permit many combinations of components. A major drawback is the difficulty of achieving uniform dispersion without excessive agglomeration of dispersed phases; this tends to inhibit achievement of fineness of particle and uniformity of interparticle spacing. The

time required for ball milling may also be considered a drawback for this particular process.

COMMERCIAL APPLICATION OF DISPERSION STRENGTHENING

The industrial potential of the dispersion strengthening concept is colored by technical-economic considerations. The commercial producer must convince the potential purchaser that the cost of the material is competitive for the intended use and is the best possible material. This is not always easy when the producer must recover his investment in a reasonable time.

The author of this report has sought information on the manner in which the dispersion strengthening concept has penetrated industrial markets. The results, given here, demonstrate the broad spectrum of potentiality rather than the completeness of such penetration. In addition to the examples to be cited, ample evidence was found that many firms are conducting development programs of various kinds. In most cases, there was little indication that commercial status was immediately achievable, but there was considerable interest in continuing the work.

Two alloys were found to be specifically available on a commercial basis:

TD Nickel.—This nickel containing nominally 2 percent thorium oxide dispersion is available from Du Pont in the form of sheet or foil, at from \$30 to \$64 per pound depending upon thickness. It is also available from secondary sources in the form of wire or rod at sizes from 0.0005 inch to 0.5 inch, as tubing, and in a wide variety of fasteners. TD nickel is considered to have superior properties in the 1800° to 2400° F temperature range; thermal stability with no degradation of properties after 2500 hours exposure at 2100° F; high thermal conductivity, comparable to high-purity nickel; higher melting point than superalloys; excellent thermal shock resistance; and corrosion resistance better than nickel.

Suggested applications include aircraft gas-turbine components, such as turbine

vanes, burner cans, flame holders, after-burner liners; industrial furnace parts, such as heat shields, thermocouple jackets, furnace trays, torch heads, and fasteners; aerospace structures, such as heat exchangers, honeycomb panels, thrust-chamber tubing, gas control valves, and special fasteners; mechanical testing components and pull rods; and specialty cathodes in electronics.

Dispersion-hardened copper.—This is a high-conductivity copper matrix containing nominally not over 0.5 percent beryllium oxide dispersion. It is available from Handy & Harmon in rod or wire form for \$10 to \$19 per pound depending upon quantity and diameter. This alloy is considered to have superior properties at elevated temperatures, such as strength, electrical stability, and resistance to crystallization. These properties appear to make it desirable over hard-drawn copper, zirconium-copper, or beryllium-copper alloys for some purposes.

Possible applications include high-temperature conductors, such as motor windings, springs, connectors, magnet wire and cable; electronic tube structural parts; high-conductivity brazed components such as contact arms and welding electrode tips; and die-casting mold core pins.

A number of alloy systems were reported to be in the developmental stage, of which the most advanced included:

1. **Dispersion-strengthened lead alloys.**—Primarily using lead oxide as dispersant, the St. Joseph Lead Co. is developing four grades to cover a range of properties. These are being market introduced by field test in areas intended to take advantage of the augmented strength, creep resistance, and elevated temperature, where lead is desired. Potential applications include batteries, ammunition, chemical construction, architecture, radiation shielding, sound attenuation, and counterweights.

2. **Dispersion-strengthened lead and zinc alloys.**—Development programs sponsored by the industries are involved through the International Lead Zinc Research Organization. Lead alloys are being developed for

applications similar to those listed above, as well as cable sheathing. Zinc alloys are being investigated as general utility sheet for automotive appliance, electronic and other applications. Economic analysis indicates what are considered to be attractive fabricated material costs for these products.

3. *Dispersion-strengthened nickel and nickel base alloys*, produced by pressure hydrometallurgical reduction to powder feeds. This technology is being investigated by Sheerit Gordon Mines, Ltd.

4. *Dispersion-strengthened nickel and nickel-chromium alloys*, reinforced with titanium or aluminum oxide dispersion. This development, by Illikon Corp., has a proprietary selective internal oxidation technique.

5. *Lead alloys, hardened by dispersions of lead oxide and 4 percent copper*, introduced by mechanical mixing of powders, then compacted and extruded. This work is being conducted by American Smelting & Refining Co. for the International Lead Zinc Research Organization.

Other research projects not directly reported on in this survey are known through

secondary sources to be active. Institutions and systems mentioned have included:

- Aluminum Co. of America: Aluminum-aluminum oxide, aluminum-iron aluminide
- American Machine & Foundry Co.: Cobalt with various oxides, nickel with various oxides
- Curtiss-Wright Corp.: Cobalt with thorium oxide, nickel with thorium oxide, nickel-chromium with thorium oxide, tungsten with thorium oxide
- Du Pont: Thorium oxide dispersed in nickel-molybdenum and nickel-chromium alloys
- General Electric: Tantalum with various dispersoids
- Illinois Institute of Technology: Zirconium with various oxides, vanadium with various oxides
- MIT: Nickel with various oxides, copper-silicon dioxide, inconel with various oxides
- New England Materials Laboratory: Nickel-chromium with thorium oxide, cobalt-chromium with various oxides, iron-chromium with thorium oxide, iron-nickel-chromium with thorium oxide
- Nuclear Metals: Zirconium with beryllium dispersion
- University of British Columbia: Zinc-copper-titanium
- Vitro Corp.: Nickel with thorium oxide, tungsten with thorium oxide
- Westinghouse Corp.: Tantalum with various dispersoids, columbium base alloys

Fiber Composites

The rapid proliferation of the application of new ideas to the development of high-performance materials systems, specifically designed to meet extreme requirements, often has had the effect of burying the origins of the design basis as soon as sophistication sets in. The idea of using fibers—i.e., one component of a two-member composite system having a geometric restriction which limits its thickness in relation to its length—grew out of appreciation of the structural properties of bamboo. A further step, the appreciation of the utilization of the other component as a matrix which bonds the fibers for effective realization of their properties, constituted perhaps the conclusive essential element to generate the concept.

An outstanding example of an artificial advancement over the bamboo pole is the fiber-glass-reinforced plastic composite. A well-established industry now supplies structural materials to the building and transport fields where a premium is placed upon a combination of high strength and low density at normal temperatures.

The essential consideration which gives the fiber composite concept, its great potential value is the idea that loads which would produce failure of the matrix material alone can be transferred to the stronger fibrous component. The extent to which this is possible, and the degree of improvement in properties achieved, may be classified by the extensive research and engineering effort currently proceeding in this field.

PROPERTIES OF FIBERS

The fiber-glass-reinforced plastic composite, like bamboo, implicitly represents fibers which are continuous filaments. As fibers,

the materials are stronger than in the usual bulk form. In the case of glass, the tensile strength of fibers having cross-sectional areas of some millionths of a square inch exceeds 1 million psi, as compared with 6000 psi for the same material in bulk form. Handling and processing tend to reduce this surprisingly large value somewhat, but it remains in the hundreds of thousands of psi. Table 2 gives analogous values for other materials. While the impressive increase in tensile strength does not by any means represent the only consideration in the design and utilization of a composite, it does point the way to new strength properties and to the use of lightweight materials in load-bearing services not previously conceived.

TABLE 2.—*Tensile strength of various materials in fiber form*

Material	Fiber form, psi	Bulk form (average), psi
Graphite whiskers	3 500 000	2 000
Alumina whiskers	2 200 000	30 000
Iron whiskers	1 900 000	25 000
Tungsten wire	550 000	220 000
Ausformed steel	450 000	65 000
Piano wire	350 000	42 000
Fiber glass	200 000	6 000
Nylon	80 000	12 000
Aluminum	60 000	40 000
Wood	15 000	5 000

Practical realization of the concept was considerably advanced by the pioneering investigations of NASA's Lewis Research Center, where it was found that the reinforcement properties do not depend upon the factor of continuity of the fiber. The Lewis investigators found that the strengthening effect occurs with very short fibers, just as with continuous ones, provided other, very

important criteria can be met, with respect to the size, properties, and positioning of fibers. Working with tungsten wires in a copper matrix, they varied the diameter of long and short fibers. Figure 4 shows the cross-sectional structure of tungsten wires in copper. Figure 5 shows the relationship of strength to diameter of fiber at progressive increases in volume occupied by continuous fibers. Figure 6 shows that the relationship is the same for discontinuous fibers.

The conditions which support and produce this relationship include:

1. The fibers are oriented in the direction of application of the load.
2. The fibers are not allowed to touch one

another but are surrounded and wetted by matrix material.

3. The transfer of stress occurs across the interfacial surfaces comprising the wetting areas.

4. The mechanical properties are calculable, additive, and follow Hooke's law.¹

5. The fibers should be as uniform as possible in regard to strength, size, shape, orientation, and bonding.

These findings are highly significant. We now have an engineering materials concept which can be used for design purposes. The proportionality factor of stress-strain relationship is a physical property of the particular material; the additivity and production

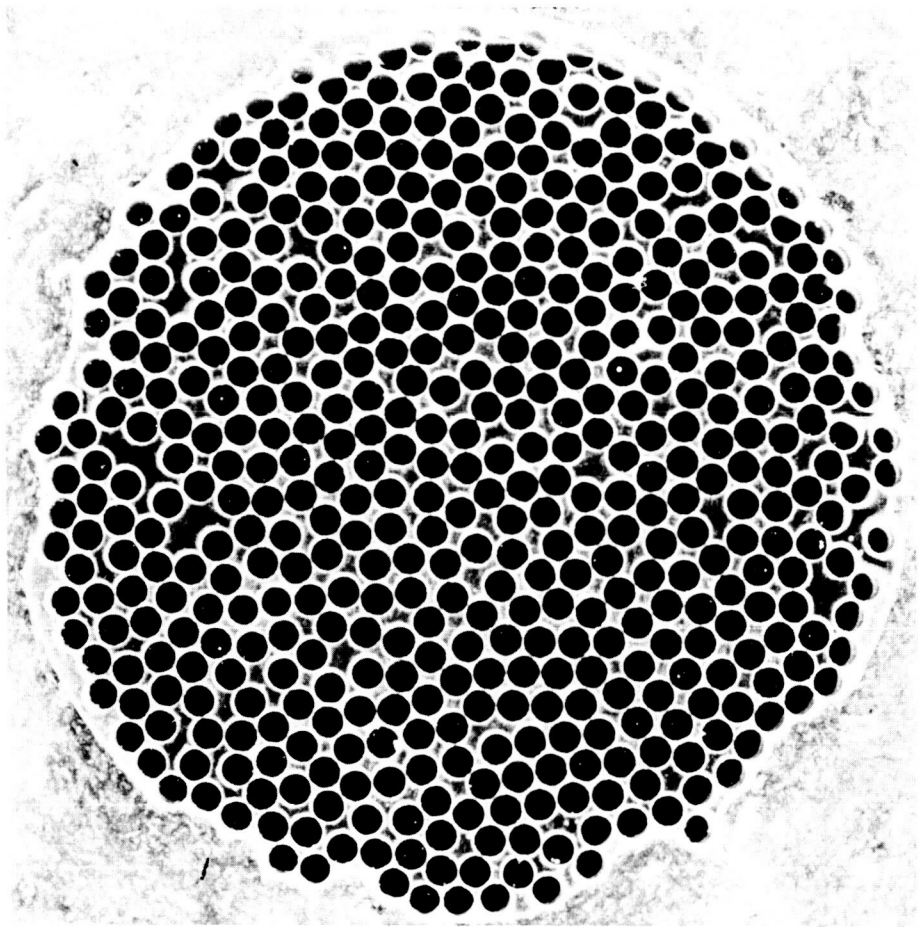


FIGURE 4.—Transverse section tungsten-reinforced copper composite composed of 483 5-mil wires. (unetched mag: 50 \times .)

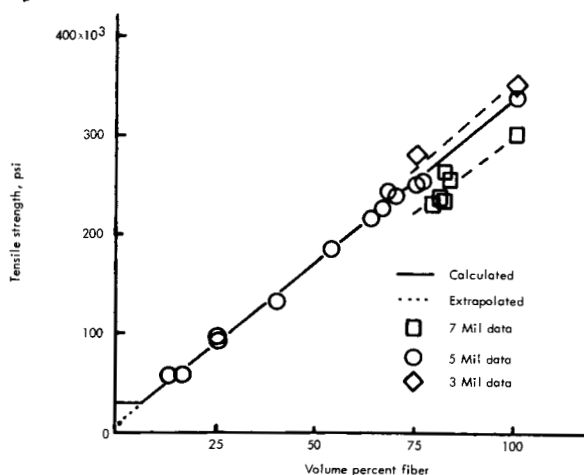


FIGURE 5.—Composites of continuous tungsten fibers in copper.

requirements are spelled out. It is now understood that some of these criteria represent idealized requirements, not always met exactly by production technology. However, the relationship is expressed by the following equation:

$$S_c = S_f V_f + s_m (1 - V_f)$$

where

S_c is the tensile strength of the composite,

S_f is the tensile strength of the fiber,

V_f is the volume fraction occupied by fibers, and

s_m is the stress in the matrix corresponding to the fracture strain of the fibers.

Since transmission of stress, when the fibers are discontinuous, occurs from fiber to fiber through the matrix, the strength properties of the matrix enter into the final result more significantly than in the case of continuous filaments. This leads to the result that the shear stress, or failure force, in the matrix cannot exceed the maximum stress in the fibers. This in turn yields a critical relationship expressed in terms of the ratio of length to diameter in the fiber. This ratio is termed the aspect ratio, and its critical

value defines the effective tensile strength of the composites. For a given diameter of fiber, the fiber length is significant; it defines the critical aspect ratio, by defining the minimum length of fiber which will produce strengths approximating those achievable by continuous fibers of the same diameter. For the case of tungsten wires in copper, the aspect ratio of 40 was required to achieve a strength of 95 percent of the continuous fiber composite.

WHISKERS

In searching out the fiber characteristics which would bring the greatest improvement in properties, especially at elevated temperatures, over the pure matrix alone, it has been known for almost a decade that the best fiber form to use is the whisker. The whiskers are very fine, single crystals of materials which have high strength and high elastic modulus, in a size range of several millimeters in length, and several microns (thousandths of a millimeter) in thickness or diameter.

To understand why whiskers are so desirable, one must accept the explanations of dislocation theory and the postulate that stipulates that near-ideal strength is the result of perfect distribution of interatomic

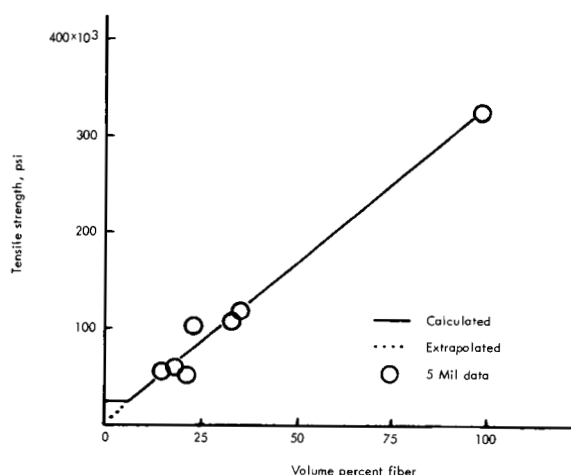


FIGURE 6.—Composites of discontinuous tungsten fibers in copper.

¹ The elastic response of a material to a deforming force is such that the strain in the material is proportional to the imposed stress.

forces, achievable by perfection in the crystal. Small crystals stand a much greater chance of being perfect. It is the uncontrollable growth of crystals during solidification which induces irregularities in the resulting solid. These irregularities take the form of vacant atom sites and of irregular interatomic distances. The strength of whiskers compared with macrocrystalline bulk properties is shown in table 2.

An example of the striking improvement of strength obtained at elevated temperatures as a result of compositing can be seen in figure 7 which shows the comparison in tensile strength of whisker and powder reinforcement, using alumina in a silver matrix.

Preparation of whiskers depends on the composition to be made. Three general classes of materials in particular should be noted:

Metal whiskers.—Iron, copper, silver, cobalt, nickel, palladium, manganese, mercury, zinc, cadmium, tin, and chromium have been produced. The principal techniques include:

1. Reduction of the metal halide in a hydrogen atmosphere at temperatures in the range of 400° to 900° C.

2. Condensation of metallic vapors under controlled conditions.

3. Solidification of a eutectic composition. (A eutectic is a solid having a composition such that upon solidification from a melt of that composition, two different solid phases are produced.)

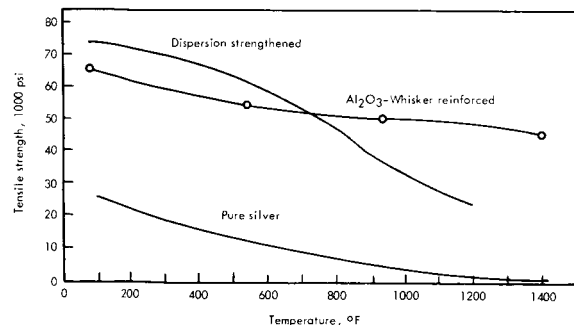


FIGURE 7.—Tensile strength of silver composites at various temperatures.

(From Fiber Composite Materials, an ASM publication.)

4. Recrystallization of a metal in bulk form.

Metalloid and intermetallic compositions.

—Carbon, silicon, boron, germanium, metallic silicides, carbides, borides, nitrides, sulfides are produced by methods generally involving decomposition of vapor compounds as well as reactions in controlled atmospheres, at relatively high temperatures, in the range of 1200° to 1700° C. A recent NASA investigation discloses a new approach: the production of fibrous filaments *in situ*, using powder metallurgy procedures, with tungsten powder forming the matrix and materials initially in nonelongated form consisting of zirconium oxide, thorium oxide, hafnium oxide, hafnium nitride, hafnium carbide, tantalum carbide, and hafnium boride. After preparation, the major processing steps include mixing, cleaning (of tungsten with hydrogen), compaction, sintering (in some cases in vacuum), and extrusion at high temperatures (3700° to 4200° F). It is interesting that relatively conventional powder metallurgical processing steps were found capable of producing a fibering effect with associated strengthening.

Oxides.—Alumina, silica, zinc oxide, molybdenum oxide, magnesia, magnesium silicate, chromium oxide, and beryllia can be made by heating the metal in an oxidizing atmosphere, cleavage, condensation, and, in the case of alumina, heating the metal in an atmosphere of moist hydrogen at 1300° to 4500° C—a procedure which points to the difficulty of foretelling the sequence of events which lead to whisker production rather than any other physical form.

The method of production, control of process conditions, and understanding of the production sequence are the source of considerable contemplation, mainly for reasons having to do with the consistency and degree of perfection, and strength of the final product. The elastic modulus of the material is the criterion of evaluation, and the degree of value is measured in terms of the percentage of that modulus which can be attained by a given method of production. The

TABLE 3.—*Calculated modulus to density rating for selected crystals*

Crystal	Modulus, million psi	Density, lb/cu in.	Fig. of Merit, million/in.	Strength, million psi
Diamond	170	0.126	1350	8.5
Carbon	82 (30)	.049	1650 (600)	4.0 (1.5)
3Al ₂ SiC	75	.091	825	3.8
B ₂ C	66	.090	734	3.3
Be	45	.065	692	2.2
SiC	71	.115	616	3.5
B	51	.083	615	2.6
TiB ₂	94	.162	580	4.7
Be ₂ C	46	.087	529	2.3
Al ₂ O ₃	76	.144	526	3.8
BeO	51	.108	472	2.6
TiC	72	.177	406	3.6
ZrB ₂	64	.202	317	3.2
MgO	35	.126	278	1.8
FeS ₂	50	.180	276	2.5
Si	23	.083	275	1.7
MoSi ₂	55	.217	244	2.8
ZrC	50	.246	203	2.5
NbC	50	.282	177	2.5
WC	104	.580	173	5.2
Steel	28	.282	99	1.7
W ₂ C	62	.625	99	3.1
W	60	.696	86	3.0

^a 30 million has been measured, 82 million is considered a reasonable expectation.

theoretical strength of a perfect crystal, expressed as a fraction of the elastic modulus, is believed to lie between 3 and 17 per cent of the modulus. L. N. Hjelm has considered a series of candidate materials of interest for aerospace application, and has evaluated them in terms of a figure of merit which rates the modulus to the density, as shown in table 3.

For materials that have been studied in depth, the following factors are known to have a profound effect upon their strength:

1. *Whisker size.* — Alumina tensile strength increases from 100 000 psi at 400-micron diameter, to more than 3 million psi at 10 microns. The relation is not linear, and the method of measurement, as related to the method of production as well as type of stress imposed, shows large changes at diameters down to, and below 2 microns.

2. *Degree of perfection.*—Here again we refer to conjecture having to do with degree of mobility of dislocations as well as their multiplicity. This also has to do with the brittleness or ductility of the material in

question—which refers in turn to the ease or difficulty with which dislocations can move through the crystals. Present thought differentiates the causes of high strength in whiskers from that in bulk materials in terms of dislocation density. In the bulk form a large number of dislocations makes for high strength, while the opposite is believed to be the case for whiskers. The techniques for observing dislocations in ultra-fine filaments are not simple, and crack formation by dislocation pileup in filaments is not clearly understood.

3. *The effects of impurities* and alloying components are generally specific and secondary. This aspect requires some further study.

4. *Temperature increase* tends to produce significant reduction in whisker strength,² as evidenced by studies made with alumina

² This should not be confused, however, with the striking effect of compositing which the use of alumina whiskers has upon the serviceability of silver, where it was observed that strengths many times that of pure silver were observed up to over 90 per cent of the melting point of the pure silver.

and with iron whiskers. The fracture stress of alumina falls off very sharply from room temperature up to 2000° C, while the yield strength of iron whiskers decreases from 1.4 to 0.6 percent of the elastic modulus as the temperature is raised to 550° C. Heating is believed to generate crack-nuclei. A further effect is delayed failure, or fracture after a time at temperature under the action of a specified load.

5. *Whisker surface condition* or exposure to a given environment will have an effect, which is essentially mechanical in nature, but not chemical. In other words, a smooth, clean surface will not show significantly better strengths, while a roughened surface will show reduction, due probably to the formation of foci of stress concentration. This can happen in the composite bonding process, which brings up the question of problems in the technology of using fibers to make composites.

PRACTICAL CONSIDERATIONS IN FIBER COMPOSITE TECHNOLOGY

Since a wide variety of types of materials may be composited, the selection of a particular combination is governed in part by what one can produce, but several additional factors must be taken into account. Unfortunately, a specified strength and toughness can be achieved only at the expense of ease of fabrication. For example, if one has to resort to relatively brittle fibers (such as ceramic compounds, oxides, etc.) for a high modulus, the limitation on fabrication which results from the limited ductility, as compared with metal fibers, is not to be overlooked. In extrusion, for example, the reduction in cross section may have to be undertaken very gradually to avoid fragmentation of the fiber; this would not occur with ductile fibers.

Sometimes it is of the utmost importance to pay close attention to the ease of wetting of the fiber and matrix. Whatever is meant by wetting (and this is a moot question), effective but not necessarily continuous contact is essential for the transmission of

stresses. Solutions to this particular problem, depending upon the empirical qualitative properties of the particular fiber-matrix combination chosen, may be found by subjecting the fibers to a preliminary cleaning step, or, in other instances, by producing a metallic coating on the fibers before infiltration of the fiber bundle with matrix material. These steps are not always necessary.

Another extremely important consideration has to do with the avoidance of fiber-fiber contact. It seems that such points of contact become the foci of cracks in the fiber as a result of abrasive action. These are propagated when the composite is loaded.

Pioneering investigations at NASA Lewis Research Center took such factors into account, and established the validity of the idea that fiber composites, whether the fibers are continuous or discontinuous, can produce predictable reinforcement.

General considerations of a mechanical and geometric nature pertaining to the desirable features of fibers and of matrices must be stressed, if the achievement of the potentials of composites is to be realized. At this stage in the advancement and generalization of the art most of these follow from an appreciation of the concept.

For example, fiber strength should be maximum, and uniformly so. It should be borne in mind that there is a significant fabrication. Fibers should be as uniformly shaped as possible, with minimal cross sections and optimum aspect ratios—optimum because, while large ratios are beneficial, short fibers are more nearly perfect and stronger. Where, as in the case of alumina whiskers, the cross section is not circular, but has crystalline orientations, data relative to the stress-bearing differences arising therefrom must be considered.

Fibers should be as perfectly aligned as possible within the matrix in the direction of application of the load, be uniformly distributed, and not overlap or touch one another.

Insofar as the matrix material is concerned, various gaps exist in our knowledge

of what constitutes the best characteristics. Since the reason for a composite is to augment and sustain the strength of the matrix, the elastic modulus and tensile strength will normally be less than that of the matrix in concept. In addition, however, the wetting action referred to above should not cause deterioration of the fiber by diffusion of one material into the other, or by corrosive chemical attack, especially at the elevated temperatures at which the strength and toughness retention is desired. Finally, a mismatch of thermal expansion properties of fiber and matrix materials can produce a weakening effect either by disruption of the integral interface, or, as observed by NASA investigators, recrystallization of the fiber as a result of temperature rise.

Another area in which attention to practical specifics must be paid, and in which problems arise, concerns the technology for the compounding of the mixture, its fabrication into useful form, and the retention of design properties at joints. Production methods depend upon the physical form in which the components are available. If we are dealing with a matrix of a refractory metal, the chances are that it will be available only in powder form and techniques of powder metallurgy will be attempted. If the matrix material can be melted, without damage to the fiber, the composite can be cast or molded by infiltration. Other means of forming a basic shape may be available. The intention is to achieve the distribution and uniformity discussed above, at the maximum (theoretical) density. The production of specific shapes will depend upon the feasibility of various fabricating steps, such as extrusion, forging, rolling, drawing, etc. As previously pointed out, successful fabrication is a matter of trial and evaluation of the properties of the composited material—but hardly more so than the determination of process limitations of a new alloy. Similarly, with respect to joining, methods involving various kinds of welding, chemical, pressure, and diffusion bonding require investigation and development, especially where mechan-

ical fastening is not the most satisfactory solution.

Problem Areas

From the discussion thus far, one may gain the impression that fiber composites represent a well-established technology and materials utilization potential, but many detailed hurdles remain.

Even though we may have a fair idea of the characteristics of fibers and whiskers which will achieve the reinforcement, it is not possible to affirm that we have general capability to produce such fibers at will, combining high strength, high elastic modulus, and high melting point. Nor can we do so with the requisite degree of uniform product quality at will, nor, as will be seen below, at commercially attractive cost.

The fiber production processes generally have low productivity and inadequate product control. Vapor deposition processes are slow and yields are low. Wire drawing can overharden the material, making it excessively brittle. There is also considerable variation in surface quality, especially as the diameter approaches 0.001 inch. This variation is very difficult to detect. In general, we know very little about the effects of handling fibers during fabrication. Nor can we make reliable predictions concerning the environmental effects upon fiber strength. It is also necessary to produce fibers in a manner which will inhibit or minimize surface defects which can act as loci for stress concentration.

Our choice of matrix materials should not be governed by wishful thinking. Although our understanding of the bulk properties of matrix metals is well advanced, and we can rely upon a large body of information on the refractory metals, matrix-fiber interactions remain rather unpredictable, as do the extension of findings from pure metal matrices to alloys—an area which is undergoing increasing examination.

Interface phenomena can have a very serious effect upon the reinforcement as the

temperature increases. For example, if two components have excessively different thermal expansion coefficients, local microcracks may inhibit the effective and uniform transmission of stress. Furthermore, the interface may act as the locus of chemical reactions, including corrosion, if these are possible between the components. Mutual dissolution can occur, and low-melting eutectic compositions may also result. All such effects weaken the system.

Physically, the misalignment and overlapping of fibers, as well as their shape, may react to disadvantage. As has been pointed out, the selection and achievement of optimum aspect ratios, as well as comparative strength and elastic properties of the fiber and matrix, must be taken into consideration.

In general, the interpretation of test data on developmental composites requires critical consideration if the reasons for failure are to be understood. Types of failure correlated with kind of service—thermal, cyclic, compression, tension, impact—must be understood in both qualitative and statistical manners. These are not only matters of concern for adequate estimation of service characteristics; they are also involved in fabrication and joining processes.

Challenges to the fiber-reinforcement composite concept include development of augmented properties at room temperature as well as elevated temperatures. The most promising materials in this category, as well as the materials receiving major attention as fibers, are listed in table 4.

Whisker Economics

Where feasibility and reliability are primary considerations, the cost may be a secondary matter—at least, until the application becomes routine. Then the financial justification assumes importance. Commercial applications, on the other hand, are nearly always evaluated immediately from the standpoint of cost and scope of market. Inevitably, the problem is reduced to what a given expenditure for a specific performance capability will buy. Composites which have been developed in this manner have proven their worth and fully justify the attitude that this materials concept can indeed become a major industry. One can see this in considering the progress in the development of composites such as automobile tires, brake linings, grinding wheels, and building materials, such as concrete.

If elevated temperature properties translate into desirable high-performance strength, toughness, and creep-resistant systems in the future, it is not at all unlikely that the advanced materials will ultimately justify their use sufficiently to bring about volume production and cost reduction.

In this developmental phase of whisker composite technology, prices are mentioned only to indicate that further development goals are justified, and that some commercial production is available. The following quotations were received from various companies:

- Boron filaments:
\$6000/lb.
\$1000 or \$2000 per lb.
As low as \$250 per lb.

TABLE 4.—Strength properties of various whiskers

Material	Ratio modulus density, millions psi	Ultimate tensile strength, 1000 psi	Melting point, °C
Graphite whiskers	1900	3000	3700
Boron filaments	795	350-1000	2200
Boron carbide whiskers	715	965	2450
Beryllium wire	630	220	1285
Silicon carbide whiskers	560	100-1650	2700
Beryllium oxide whiskers	550	2000-2800	2550
Alumina whiskers	440	160-2600	2000

- **Aluminum oxide whiskers:**

Scaling would reduce the price to about \$3 per pound.

Sapphire whiskers at \$15,000 per pound, to \$5,000/lb. within a year, to \$100/lb. by 1970, \$10/lb. by 1980, . . . and an eventual price of \$1 per pound.
- **Metal filaments:**

Metal filaments as small as 1 micron in diameter are now being offered at \$25-\$50/lb. in laboratory quantity (stainless steel). This price is expected to drop to \$5-\$10/lb. with increasing production.
- **Silicon carbide whiskers:**

Silicon carbide whiskers can now be purchased in 25-lb. lots at \$750/lb. If sufficient volume can be developed, price is expected to be drastically reduced.
- **Boron nitride filaments:**

One company offers this product at \$175 per pound, ultimately expects to sell in quantity below \$10/lb.
- **Metal filaments:**

One company offers the following compositions:
Type 304 stainless steel, 25 to 4 microns, at \$20 to \$47.50 per pound depending upon diameter.
Super alloy, nickel base, age hardenable, 12 micron at \$210 per pound; 6 micron at \$325 per pound.
Niobium, 12 microns to 3 microns at \$1350 to \$2150 per pound depending upon diameter.
Tantalum, 12 microns to 3 microns at \$950 to \$1500 per pound depending upon diameter.
- **Graphite fiber filaments:**

One company offers a high strength, high modulus of elasticity graphite filament for high performance composites, at \$500 per pound.

Reinforced Ceramics

No survey of composites would be complete without consideration of the possibilities of the use of ceramic matrices. There are compelling reasons for this, especially for adaptability to high-temperature service under conditions requiring structural stability and resistance to environmental attack. Most ceramics of conventional composition are oxides of one kind or another, such as aluminum oxide, beryllium oxide, and magnesium oxide. If properly designed, they may have extreme stability in oxidizing environments and may withstand considerable stress and shock conditions. The strength of such ceramics can be available when the component is in compression even though the material is very weak when in tension or when subjected to high impact or thermal shock.

The hope of utilization of the composite concept centers about the possibility of strengthening the ceramic body by attempting to use it as a matrix for a high-strength, high-modulus fiber. This is difficult because the modulus of elasticity of ceramics is very high to begin with, while tensile strengths are low. This combination makes the transmission of strains to the fibers embedded in ceramic matrices very difficult; the matrix may crack and rupture before a significant fraction of the load is transmitted. There are, furthermore, not too many materials of a nonceramic nature which could be likely candidates for use as fibers; which have the required characteristics, particularly a sufficiently high modulus to contribute to a strengthening mechanism. Prestressing, as in the case of structural concrete containing prestressed reinforcement steel rods, can often be considered. In this case, the

enhancement of reinforcement would be obtained by making the composite in a thermal cycle which introduced the stressed state into the fiber upon cooling. The fiber, however, must have thermal expansion properties equivalent to those of the ceramic matrix or better, and as usual, an adequate bond must be effected between the ceramic and the metal fiber at the interface. The incentives for developing such composites are fairly compelling, especially where it has been established that reinforcement is significant, as in the ability of the body to withstand thermal or mechanical shock. In this regard, it has been established that, with good bonding and adequate incorporation of fibers, it is possible to inhibit catastrophic failure of the ceramic; the fibers act to retard destructive cracking.

FILLERS

To accomplish this type of strengthening, the metallic reinforcement material is introduced in a variety of forms: laminations, fibers, mesh or expanded metal, and metal wool. With the exception of fibers, it is apparent that some degree of continuity is required of the metal. The lamination involves using the metal as a substrate, and applying the ceramic as a coating over it. This is the concept of a simple surface with a planar interface. This form is frequently considered where a metal surface requires protection against high-temperature environmental attack for structural service. The integrity of the coating is all-important, and design considerations as well as chemical resistance play an important role, whether the structure is in tension or in compression, and whether the environment has a corrosive

action due to aerodynamic oxidation or to the chemical composition of a combustion mixture. The uses of ceramics as coatings is a subject in itself, and comprises an important part of the aerospace technology. The use of high-temperature refractory alloys hinges upon the ability to develop adequate protective coatings. The reentry problem, for a long time, consisted in finding a composite which would furnish adequate thermal protection and oxidation resistance at very high temperatures; the properties of oxides such as silica and magnesia became significant. Other coating materials, of a more sophisticated nature, such as silicides and aluminides, represent efforts to achieve higher service temperatures for longer periods under corrosive conditions.

A commercial example of the simple coated composite has been developed to a high degree of applicability in the chemical process industries. Depending upon the application intended, a ceramic is matched to a metal substrate; that is, the ceramic has slightly lower thermal expansion than the metal, so that the ceramic coating is in compression on cooling. Furthermore, the ceramic is deliberately produced so as to avoid a glassy composition. Instead, it is made to have a crystalline character—which gives greater mechanical strength, thermal shock resistance, and corrosion resistance, all at significantly higher temperatures, up to about 1500° F. The metals used include some of the more refractory alloys, steels, Inconel, titanium, columbium, and molybdenum. However, the baser metals and certain stainless steels cannot be used; the former have too much carbon, while the latter have high expansion coefficients. The application of columbium and other high-temperature alloys may lead the way to methods of using coated components in high-temperature gas turbines and combustion chambers.

A logical extension of the simple substrate-coating concept is the use of perforated, honeycomb, mesh, grid, and expanded metal reinforcement systems, which are filled by troweling, casting, ramming, or otherwise filling the metal skeleton, and then curing and firing the aggregate. This is in contrast to the simple coating techniques, which may involve spraying and heating, flame-spraying, even plasma spraying methods. Other coating techniques include pack-cementation and chemical vapor deposition.

The use of continuous filaments such as metal wool, involves felting the wool and then slip casting the ceramic slurry into it, while short fibers can be slip cast or pressed, hot or cold as needed, and then fired.

The reinforcement techniques of ceramics by composite formation is a highly empirical art at present, and requires further investigation.

THE CURRENT TREND

Engineering advancement in the field of materials is generally conceded to be arduous. The materials "bottleneck" in our aerospace effort is universally recognized. Much of the difficulty arises from attempts to deal with environmental challenges by classical approaches. Now a trend in positive thought concerning the possibility of designing materials more purposefully and finding how to combine them phenomenologically to perform exotic and unconventional functions has appeared. The concept of composites is a pioneering product of such thinking. It signifies a more rational use of resources and disciplines for the attainment of difficult technical and economic goals, and deserves the most serious and protracted consideration in every phase of technology related to our national economy.

Bibliography

Articles listed here were chosen for their usefulness in orienting the reader in three basic categories:

(1) sources of fundamental discussion and definitive treatment of pioneer efforts. These are mainly reviews and expositions of basic underlying principles; (2) a compendium of titles drawing on NASA-sponsored and NASA-generated programs, especially those having significant bearing upon the development of principles, materials systems, and applications; and (3) examples of sources of composites and materials of the type required to produce them. These have been limited to the materials categories covered in this report. The field of plastics composites is well established and commercial sources are available in the usual channels.

In a field undergoing development and recognition as rapidly as this one, omissions and changes are unavoidable. It is hoped that these have been kept to a minimum.

SOURCES OF FUNDAMENTAL DISCUSSION

- American Society for Metals: Fiber-Composite Materials. Seminar of ASM, Oct. 1964. Am. Soc. for Metals, 1965.
- BUNSHAH, R. F.; AND GOETZEL, C. G.: A Survey of Dispersion Strengthening of Metals and Alloys. WADC Tech. Rept. 59-414, 1960.
- DIETZ, A. G. H.: Fibrous Composite Materials. Int. Sci. and Tech., Aug. 1964, p. 58.
- HIBBARD, WALTER R., JR.: Composites: Materials of the Future. Chemical Engineering, Nov. 11, 1963, p. 203.
- HJELM, L. N.: Metal-Ceramic Composite Structural Materials. Section in Air Force Materials Symposium. AFML-TR-65-29, May 1965, pp. 555-582.
- JECH, R. W.; WEBER, E. P.; AND SCHWOPE, A. D.: Fiber-Reinforced Titanium Alloys. Reactive Metals. Interscience Pub. (New York), 1959.
- LESZYNSKI, W., ED.: Powder Metallurgy, Section on Dispersion Strengthening. Interscience Pub. (New York), 1961, pp. 283-285.
- Materials in Design Eng., vol. 58, no. 3, Sept. 1963, pp. 79-126.
- The Promise of Composites. Materials in Design Engineering Special Report no. 210.

WEETON, J. W.; AND SIGNORELLI, R. A.: Fiber-Metal Composites. 12th Sagamore Army Materials Research Conf. NASA TM X-52123, Aug. 1965.

PUBLICATIONS CITING NASA-SPONSORED WORK

- CREMENS, W. S.: Use of Sub-Micron Metal and Non-Metal Powders for Dispersion Strengthened Alloys. Electrochemical Society Symposium, 1961.
- DIERSING, R. J.; CARMICHAEL, D. D.; HANES, H. D.; AND HODGE, E. S.: Diffusion Bonding of Stainless Steel Wire Mesh Reinforcement to Beryllium Tube for Hypervelocity Impact Target. NASA CR-54222, 1964.
- GATES, L. E.; LENGT, W. E.; AND TEAGUE, W. T.: Ceramic Fibers for Reinforcement in Composite Materials. NASA CR-50793, 1961.
- GRIERSON, R.: Elastic Strains Associated With Particle-Matrix Interface in Certain Dispersion Strengthened Alloys. NASA CR-60225, 1964.
- GRISAFTE, S. J.; AND SPITZIG, W. A.: Metallurgical Bonding between Plasma-Sprayed Tungsten and Hot Tungsten Substrates—Interface and Recrystallization. NASA RP-41, 1963.
- GRISAFTE, S. J.: Shear Bond Strength and Alumina Coatings. DMIC Memorandum 204. Summary of 10th Meeting of Refractory Composites Working Group. Defense Info. Metals Center, Battelle Mem. Inst., 1965.
- HASHIN, Z.; ROSEN, B. W.; AND DOW, N. F.: Mechanical Properties of Fibrous Composites. NASA CR-51169, 1963.
- HEDGEPEETH, J. M.: Stress Concentrations in Filamentary Structures. NASA TN D-882, 1961.
- HOPKINS, J. M.: Elimination or Control of Fiber Orientation for Improved Fatigue Life of Steel Ball Bearings. NASA CR-55402, 1963.
- HUFFMAN, J. W.: Composite Materials Development for Shell Structure of Launch Vehicle Tanks Containing Pressurized Fluid Propellants. NASA CR-60827, 1965.
- JECH, R. W.; MCDANELS, D. L.; AND WEETON, J. W.: Composite Materials and Composite Structures. Sixth Sagamore Ordnance Materials Research Conf., 1959.
- KELLER, D. V., JR.: Adhesion Mechanisms Between Solid Metal Surfaces. NASA TN D-2228, 1964.
- KELLER, D. V., JR.: Adhesion Between Atomically Clean Metallic Surfaces—Surface Energy and

- Bonding. NASA CR-52482, 1962.
- KUHN, W. E.; AND WOODWORTH, V. C.: Boron Carbide Fiber Production by Continuous Coating Technique and Physical Properties of Boron Carbide. NASA CR-60498, 1965.
- LACHANCE, M.; THOMPSON, B.; TODD, H.; AND KUSKEVICS, G.: Composite Ionizer Materials—Effect of Secondary Additions to Tungsten Powder on Sintering Mechanisms and Heat Stability of Porous Structures. NASA CR-54188, 1965.
- MANNING, C. R., JR.; AND ROYSTER, D. M.: Mechanical Properties and Metallurgical Character of Cr and MgO Composites. NASA TN D-1785, 1963.
- MAYER, N. J.: Structural Applications for Advanced Composite Materials. Tech. Rept. no. P 5-5-64. Am. Soc. for Metals, 1965.
- MCDANELS, D. L.; JECH, R. W.; AND WEETON, J. W.: Stress-Strain Behaviour of Tungsten-Fiber Reinforced Copper Composites. NASA TN D-1881, 1963.
- NASA TECH BRIEF: Boron Carbide Whiskers Produced by Vapor Deposition. B65-10261, 1965.
- PETRASEK, D. W.; AND WEETON, J. W.: Alloying Effects on Tungsten-Fiber Reinforced Copper Alloy or High Temperature Alloy Matrix Composites. NASA TN D-1568, 1963.
- PETRASEK, D. W.; AND WEETON, J. W.: Alloy Effects on Room Temperature Tensile Properties and Microstructure of Tungsten-Fiber Reinforced Copper Alloy Composites. NASA RP-311, 1964.
- QUATINEZ, M.; WEETON, J. W.; AND HERBELL, T. P.: Studies of Tungsten Composites Containing Fibered or Reacted Additives. Preprint no. 40(G). Int. Powder Metallurgy Conf. AIME-MPIF. June, 1965.
- QUATINEZ, M.; WEETON, J. W.; AND HERBELL, T. P.: Stress Rupture Strength Improvement of Tungsten Compositized Materials Containing Fibered or Reacted Additives. NASA TN D-2757, 1965.
- QUATINEZ, M.; SCHAFFER, R. J.; AND SMEAL, C.: The Production of Sub-Micron Metal Powders by Ball-Milling With Grinding Aids. Trans. AIME, 1960.
- RENSSELAER POLYTECHNIC INSTITUTE: Mechanical Properties of Polymers, Phase Particles in Dispersion Strengthened Alloys, Molecular Structure Relation in Polymer Flow and Dispersions, and Ceramics Research. NASA CR-59605, 1964.
- ROSEN, B. W.: Mechanics of Composite Strengthening. Ch. 3 in Fiber Composite Materials. Am. Soc. for Metals, 1965.
- ROSEN, B. W.: Failure Modes of Filament Reinforced Materials Including Influence of Constituent Geometry and Properties. NASA CR-55192, 1964.
- ROSEN, B. W.; DOW, N. F.; AND HASHIN, Z.: Mechanical Properties of Fibrous Composites. NASA CR-60668, 1965.
- ROSEN, W. B.; ET AL: Mechanical Properties of Fibrous Composites. NASA CR-31, 1964.
- SCHAFFER, R. J.; QUATINEZ, M.; WEETON, J. W.: Strength and High Temperature Stability of Dispersion Strengthened Nickel-MgO Alloys. Trans. AIME, 1960.
- SCHUERCH, H.: Compressive Strength and Failure Modes of Boron Fiber-Magnesium Matrix Composite. NASA CR-202, 1965.
- SINCLAIR, J. H.; AND BYORGAK, C. A.: Effects of Two Nickel Alloy Braze Coatings, Heat Treatments, and Processing Variables on Rupture Strength of Sheet Metals. NASA TN D-1880, 1963.
- STYRH, K. H.; HESSINGER, P. S.; AND RYSHKEWITCH, E.: Matrix and Composite Materials of Zirconium Oxide, and MgO With Tungsten-Protective Coatings for Thermal Insulations. NASA CR-50877, 1963.
- TETELMAN, A. S.: Investigation of Strengthening and Fracture in Composite Materials. NASA CR-60123, 1964.
- TSAI, S. W.: Strength Characteristics of Anisotropic and Laminated Composite Materials. NASA CR-224, 1965.
- TSAI, S. W.: Structural Behaviour of Composite Materials. NASA CR-71, 1964.
- TSAI, S. W.: Structural Behaviour of Laminated Anisotropic Plates: Cross-Ply and Angle-Ply Composites. NASA CR-56343, 1964.
- TSAI, S. W.: Composite Moduli of Unidirectional Fiber-Reinforced Media. NASA CR-52410, 1963.
- WASHINGTON, A. A.: Effect of Three Metal Additions on Grain Size of Magnesium Oxide After High-Temperature Heat-Treatments. NASA TN D-2823, 1965.
- WASHINGTON, A. A.: Effects of Several Metal and Compound Additions on Grain Growth of Oxides. NASA TN D-2820, 1965.
- WITUCKI, R. M.: Boron Filaments. NASA CR-96, 1964.

COMMERCIAL SOURCES OF COMPOSITES AND COMPOSITE MATERIALS

- TD nickel: thoriated nickel alloy:
E. I. duPont de Nemours & Co., Inc.
Wilmington, Del.
- Cube alloy: dispersion hardened copper-beryllium oxide alloy:
Handy & Harmon
New York, N.Y.
- Zirconium-beryllium alloy in limited quantities:
Nuclear Metals Division
Textron, Inc.
West Concord, Mass.
- Sapphire whiskers:
Thermokinetic Fibers, Inc.
Nutley, N.J.

Single crystal silicon carbide fibers in limited quantities:

Carborundum Co.
New Products Branch
Niagara Falls, N.Y.

Boron filaments:

Texaco Experiment Co.
Richmond, Va.

Stainless steel nickel-base superalloy and refractory metal filaments:

Brunswick Corp.
Chicago, Ill.

DiPac: dispersed composites, aluminum, copper, and stainless-steel matrices for silicon carbide, aluminum oxide, graphite, and Teflon dispersoids:

Avco Corp.
Industrial Products Subdivision
North Wilmington, Mass.

Thornel 25: a graphite fiber filament:

Union Carbide
Carbon Products Division
New York, N.Y.